

TANNING WITH GLUTARALDEHYDE

I. RATE STUDIES*

ABSTRACT

In this study the tanning properties of glutaraldehyde were evaluated under various conditions and compared with results obtained using other aldehydes under the same conditions. Whole sheepskins (Syrian) were used in this investigation. Measuring the disappearance of glutaraldehyde from the tanning liquor provided a sound basis for evaluation of the over-all rate of tanning and fixation. Tanning was effected over a wide range of conditions. The rate of tanning and uptake of glutaraldehyde increased rapidly with increase of pH and concentration. Maximum shrink temperature also was attained rapidly and, in the higher pH ranges, was reached in about one hour. Tanning was effected with as little as 1.5% (based on the drained pickled weight) of active aldehyde. Under certain conditions complete exhaustion of glutaraldehyde could be obtained from the tanning liquors. This behavior is in marked contrast to that observed in the case of formaldehyde or glyoxal. Under comparable conditions of tanning with these three aldehydes the rate of tanning increased in the order: glyoxal, formaldehyde, and glutaraldehyde.



INTRODUCTION

The availability in recent years of several new aldehydes, particularly dialdehydes, has stimulated research to investigate the tanning action of these new members of this important and reactive class of organic compounds (1-3). Formaldehyde has been by far the best known aldehyde as regards tanning action. The formaldehyde-collagen reaction has been studied extensively, and considerable information concerning this reaction has been published. Its importance in leather chemistry is clearly evident from the

*Presented at the Fifty-fifth Annual Meeting of the ALCA at Mackinac Island, Michigan, June 14-17, 1959.

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many review articles appearing in the literature (4-8). Recent research in our laboratory (2) indicated that glutaraldehyde possessed versatile tanning power and appeared to be in the class with formaldehyde as regards reactivity. In view of the commercial availability of glutaraldehyde at relatively low cost, further study of its tanning action was most desirable. In this paper is reported a detailed study of the theoretical and practical aspects of the interaction between hide substance and glutaraldehyde. In these studies we chose to use an entire skin instead of hide powder or small pieces, in order more nearly to approach tannery practice and to enable a preliminary evaluation of the process, particularly in comparison with formaldehyde.

EXPERIMENTAL

Apparatus, chemicals, and skins.—The tanning experiments on one skin at a time were run in a small drum (approximately $17\frac{1}{2}$ " inside diameter, 8" wide) at a speed of 10 rpm. The drum was held at 84° to 88° F. in a thermostatically controlled enclosure. A time-clock and switch arrangement allowed the drum to turn continuously from 8:00 A.M. to 5:00 P.M. and then intermittently ($\frac{1}{2}$ hour on, $\frac{1}{2}$ hour off) the remaining hours of a 24-hour period.

The glutaraldehyde used in these experiments was a 25% aqueous solution available commercially. The glyoxal used was a specially purified grade free of formaldehyde and ethylene glycol. The formaldehyde used in several runs was the standard N.F. (37%) grade. The various salts used in the experiments described were of standard laboratory quality. All skins were commercial, degreased, pickled Syrian sheepskins.

Tanning procedure for rate studies.—The following is an outline of a typical tanning run using glutaraldehyde (25% commercial solution). All quantities are based on the drained pickled weight of the skin (DPW).

The pickled skin was added to a solution consisting of water (100%), Na_2SO_4 (10%), or NaCl (6%) and glutaraldehyde solution (variable from 6 to 24%). The drum was rolled for $\frac{1}{2}$ hour. At this time a shrinkage temperature (T_s) specimen was cut from the neck area of the skin, and a 5-ml. aliquot of the tanning liquor was removed for analysis and pH determination.

Since the water present in the wet skin dilutes the tanning solution, this short drumming in the pickled condition was necessary to equilibrate or uniformly distribute the water-soluble components in the aqueous phase of the system. Although there was some fixation of aldehyde in the pH near 2, the amount in the first half hour was slight (Fig. 1). Thus, analysis of the aliquot after this half-hour treatment of the pickled skin provided a reasonably accurate estimation of the initial aldehyde concentration.

TABLE I
EFFECT OF TANNING VARIABLES ON UPTAKE OF ALDEHYDE

Exp. No.	Aldehyde %	Tanning Solution*		pH†	Initial‡	Aldehyde Content of Tanning Soln., g/100 ml.				
		Buffer System				1 hr.	2 hr.	4 hr.	8 hr.	24 hr.
Glutaraldehyde, 25% solution										
1	6	NaCl, Na ₂ SO ₄ **		2.4-2.6	0.82	0.72	0.70	0.62	0.50	0.37
2	10	"		2.5-2.7	1.29	1.17	1.13	0.97	0.84	0.65
3	12	formate, NaCl		4.1	1.46	0.96	0.79	0.62	0.51	0.38
4	24	"		3.9-4.1	2.96	2.32	2.16	2.09	1.98	1.84
5	6	acetate, NaCl		4.9-5.1	0.88	0.35	0.25	0.19	0.13	0.09
6	12	"		5.0	1.63	0.92	0.77	0.74	0.64	0.51
7††	"	"		4.8	1.03	0.62	0.55	0.49	0.45	0.39
8	24	"		5.0	3.11	2.23	2.11	1.98	1.89	1.69
Blank	12	"		4.5	1.78	1.73	—	1.75	1.71	1.73
9	6	borax, NaCl		6.1-6.5	0.85	0.12	0.08	0.06	0.05	0.05
10	"	" Na ₂ SO ₄		6.2-6.7	0.78	0.11	0.06	0.04	0.03	0.03
11	12	"		6.4-6.7	1.47	0.51	0.39	0.29	0.22	0.15
12	24	"		6.1-6.5	2.86	1.82	1.62	1.56	1.37	1.25
Blank	12	"		6.4-6.6	1.86	1.78	—	1.79	1.78	1.81
13	6	NaHCO ₃ , NaCl		7.5-8.3	0.83	0.10	0.06	0.04	0.03	0.02
14	"	" Na ₂ SO ₄		7.9-8.4	0.87	0.06	0.03	0.02	0.02	0.01
15	12	"		7.6-8.4	1.50	0.44	0.26	0.14	0.09	0.07
16	24	"		7.6-8.2	2.86	1.69	1.49	1.36	1.19	0.96
Blank	12	"		7.2-8.0	1.73	1.69	—	1.70	1.67	1.54
17	6	NaHCO ₃ +MgO, Na ₂ SO ₄		9.4-9.8	0.75	0.02	0.02	0.02	0.01	0.01
18	12	"		9.2-9.6	1.55	0.24	0.12	0.09	0.06	0.05
19	24	"		9.0-9.7	2.79	1.16	0.66	0.54	0.37	0.24
Blank	12	"		9.2-10.1	1.83	1.60	—	0.61	0.35	0.23

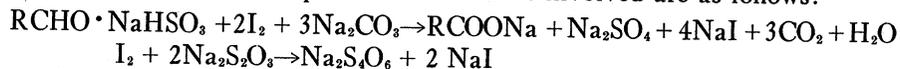
At the end of this half-hour equilibrating period the solid buffering agent was promptly added in one feed, for example, NaHCO_3 (5%), and the drum was started in motion again. The above sampling procedure, i.e., Ts specimen from neck area and 5-ml. aliquot of tanning solution, was repeated at intervals of 1, 2, 4, 8, and 24 hours after addition of the buffer. The Ts specimens were washed for 2 hours, and the shrinkage temperature was determined.

Variations in this tanning procedure were concerned usually with the use of several different aldehydes, concentration of aldehyde, and the pH (type of buffer) of tanning. In the experiments where other aldehydes (formaldehyde or glyoxal) were used in place of glutaraldehyde, the quantity of active aldehyde equivalent to that in 12% commercial glutaraldehyde solution (based on the drained pickled weight) was calculated. This amount was then used in these comparison experiments, so that the concentrations of aldehyde or active groups were equivalent in each case. The various tanning variables investigated and the results obtained are summarized in Table I and Figs. 1 to 10.

To determine the effect on the aldehydes of the buffer and salts at the various pH levels of these tanning experiments, several "blanks" or controls were carried out. These blank runs duplicated the tanning run corresponding to the use of 12% glutaraldehyde (based on the drained pickled weight) or its equivalent of other aldehyde, except that the skin was absent. Water and acid approximating that which would have been introduced with the stock were allowed for, and the same buffering systems as in the tanning run were used. This solution was agitated by drumming, and samples were periodically withdrawn and analyzed for aldehyde content exactly as those from the tanning counterpart. These results which show the stability (or lack of stability) of the aldehydes under the various tanning conditions are also included in Table I and the various figures.

At the end of 24 hours of tanning, the full skins from this rate-of-tanning study were thoroughly washed and prepared for conversion into finished leather as described in a later section.

Determination of aldehyde content of solutions.—*General:* The method of analysis selected was a modification (9) of the iodimetric method of Romijn (10). This method is based on measuring the amount of aldehyde fixed by sodium bisulfite. This reagent, used in excess, reacts rapidly with aldehydes to form relatively stable complexes. Excess bisulfite is destroyed with iodine, and a measured excess of iodine and alkaline buffer quantitatively oxidizes both the bisulfite and aldehyde moieties of the complex. Excess iodine is then determined by titration with standard sodium thiosulfate. A blank is run at the same time, and the difference in thiosulfate is equivalent to aldehyde-bisulfite complex. The reactions involved are as follows:



To test the applicability and reliability of this analytical procedure the bisulfite complexes of glutaraldehyde and glyoxal were prepared and re-crystallized by the procedure recommended for glyoxal (11). Sodium bisulfite formaldehyde complex was also purified in this manner. A sulfate ash analysis indicated a purity of 98.0 to 99.6% for these complexes. Solutions containing a known amount of these complexes were prepared and analyzed by this procedure. The results are shown in Table II.

TABLE II
ANALYSIS OF STANDARDS

Bisulfite Complex	Aldehyde Concn., g/100 ml.	
	Found	Theory
Formaldehyde	0.222	0.224
Glyoxal	0.199	0.206
Glutaraldehyde	0.980	0.993
" (2:1 dilution)	0.493	0.497
" (5:1 ")	0.196	0.198
" (10:1 ")	0.098	0.099

Analysis of tanning solutions: The samples periodically withdrawn from the tanning solution were filtered into small glass-stoppered bottles. From these bottles were pipetted the one-ml. samples used in the analysis. At times, some samples required dilution before analysis. This was true whenever the analysis indicated the tanning solution to be more concentrated than about 0.10 millimoles of aldehyde/ml. for the dialdehydes and about 0.25 millimoles of aldehyde/ml. for formaldehyde. In these cases one ml. of the tanning solution was diluted to 5 ml. (in a volumetric flask), and one ml. of the diluted solution was employed. The details of the analysis procedure were as follows:

Each analysis and blank was run in duplicate, using calibrated pipets, burets, and volumetric flasks.

One ml. of filtered tanning solution was pipetted precisely into a 125-ml. Erlenmeyer flask. Then 10 ml. of distilled water were added, and this was followed by 5 ml. of approximately 0.1N NaHSO₃. A reaction time of 15 minutes was allowed, and then 10 drops of starch solution were added as indicator. Next, iodine solution (approximately 0.1N) was added carefully to the end point to destroy excess bisulfite. When the end point was reached, exactly 10 ml. of the same iodine was added by pipet. Then 5 ml. of Na₂CO₃(2N) solution were added, and the flask was covered and placed in the dark (cabinet) for 20-30 minutes. Next, 10 ml. H₂SO₄(1N) were added (one drop was checked on indicator paper to be sure reaction mixture was acidic), and the flask was replaced in the dark for an additional 10 minutes.

The entire contents of the flask were then carefully titrated with sodium thiosulfate (0.1000*N*) to the end point.

Simultaneously a blank was run, exactly as described above except for omission of the tanning solution. Thus, only the thiosulfate need be standardized and enters into the calculations as follows:

$$\frac{N(V-V^1)}{4A} = \text{millimoles of aldehyde in sample}$$

N = normality of thiosulfate

V = volume of thiosulfate to titrate blank

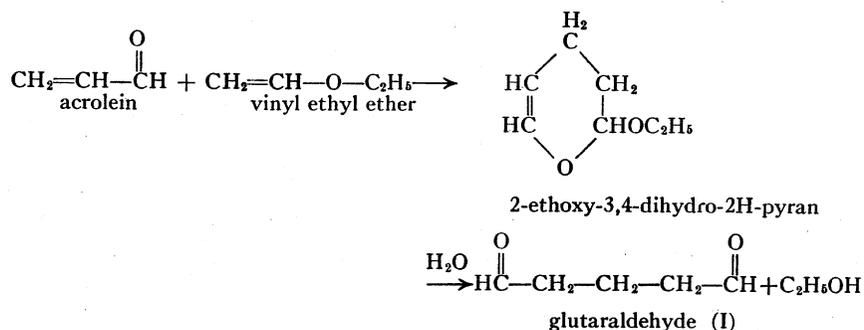
*V*¹ = volume of thiosulfate to titrate sample

A = number of aldehyde groups in molecule

The procedure outlined above was followed in analyzing tanning solutions at pH 5 or below. Samples from tanning solutions with a pH above 5 were acidified. This was done immediately after the addition of 10 ml. of distilled water mentioned at the beginning of the above analytical procedure. The acid (1*N* H₂SO₄) was added dropwise to a pH of 4. The number of drops of acid required was determined on a separate accurately measured sample, using a pH meter. The acidified samples were then analyzed as described above. The results are shown in Table I and Figs. 1 to 10.

DISCUSSION

Glutaraldehyde is a five-carbon dialdehyde of relatively simple structure (I) commercially available as a stable 25% aqueous solution. It was first reported by Harries (12) in 1908 but remained a laboratory curiosity until recent years when feasible processes were developed for its preparation. A recent publication (13) outlines the synthesis of glutaraldehyde, based on acrolein, in a two-step process. Acrolein is interacted with vinyl ethyl ether in a typical Diels-Alder reaction to produce an ethoxy dihydro pyran. This latter is then hydrolyzed with water to form glutaraldehyde and ethanol. This synthesis is outlined below:



Because of its ready availability and chemical reactivity, glutaraldehyde is a new product of the chemical industry which shows promise.

In our previous study, an estimate of the tanning power of glutaraldehyde and its comparison with other aldehydes was based on shrinkage temperature data obtained with small pieces. This, at best, was qualitative, and it was necessary to collect more scientific data concerning the rate of tanning. For this purpose it was decided that the rate of disappearance of aldehyde in the tanning liquor offered the most elegant and simplest approach to the determination of the over-all tanning rate. It was further desirable to use an entire skin in these studies in order to provide data more valuable to the tanner than similar data obtained with hide powder or small pieces of skin. This approach offers further advantage in averaging the factors of variability of the skin and enables interpretation of results from a theoretical as well as practical standpoint.

In these studies, therefore, an entire degreased pickled Syrian sheepskin of commerce was tanned with glutaraldehyde with pH and concentration as the principal tanning variables. Comparisons were made with formaldehyde and glyoxal. No pretense is made that these data are directly translatable to tannery-scale operations, since other well known factors such as mechanical action and buildup of heat enter into consideration. However, comparisons within experiments are justified.

A striking feature of the data in Table I is the rapid disappearance of glutaraldehyde and its approach to complete exhaustion when tanning was carried out under certain conditions. The data in Table I were calculated to give the percent of unreacted glutaraldehyde, and this was plotted against time to give the curves shown in Figs. 1 to 10. An advantage of the plot in this form is that fixed aldehyde expressed as percent of the drained pickled weight is readily calculated. The slope of these curves can be interpreted as a measure of the rate of tanning. In these figures the rate of change in T_s is also shown.

The rate of tanning at pH of about 2 was relatively slow, and as shown by Fig. 1 only about 5% of the glutaraldehyde was fixed in the first half hour. Thus, equilibrating the pickled skin for $\frac{1}{2}$ hour before determination of the initial aldehyde concentration introduced only a small error (of the order of 5%). Interestingly enough, half of the glutaraldehyde charged was fixed by the skin in 24 hours, and T_s was gradually raised to 70°-75°C. even at this low pH.

The rate of tanning, as expected, increased rapidly with increase of pH, as indicated by the slope of the curves in Figs. 1 to 6. The maximum shrinkage temperature also was rapidly attained, and at the higher pH range (Figs. 5 and 6) was essentially reached in one hour. In general, fixation of aldehyde continued beyond this point but did not appear to contribute to

elevation of the shrinkage temperature. In the pH range of 4 to 5 (Figs. 2 and 3) equilibrium was not reached in the 24-hour period studied, although in the case of the lowest concentration (6% of the drained pickled weight and pH of 5) 90% of the glutaraldehyde was consumed in 24 hours. In the case of 6% glutaraldehyde, exhaustion of the glutaraldehyde was practically complete at pH 6 and above. At the 12% glutaraldehyde level, uptake of the aldehyde at pH above about 6.5 was 90 to 97% of that charged.

The rate of tanning in the pH region of 9 to 10 was complicated by disappearance of glutaraldehyde due to pH effects alone as shown by the blank in Fig. 6. Thus, in the blank run, half of the glutaraldehyde was destroyed in 3 hours at this pH.

In the comparable tanning run (12% glutaraldehyde in Fig. 6), disappearance of glutaraldehyde was extremely rapid, and the rate of tanning was evidently considerably higher than the rate of destruction of glutaraldehyde. Thus, purely from the rate standpoint, tanning took preference over the side reactions despite the relative instability of glutaraldehyde under these conditions. As shown in Fig. 8, glyoxal was less stable than glutaraldehyde under these pH conditions. The instability of glyoxal in alkaline solutions is well known and is discussed by previous investigators (1, 14, 15). Under the conditions of our experiments, half of the glyoxal disappeared in 2 hours at pH of 9 to 10. These two aldehydes were stable in the pH region below about 8, and formaldehyde was stable at all pH values (4.5 to 10.5) investigated.

Figure 7 shows the rate of tanning data obtained with formaldehyde when the concentration, on an aldehyde basis, was equivalent to 12% glutaraldehyde. On a molar basis the concentration in the case of formaldehyde corresponded to twice that of the glutaraldehyde. The important conclusion drawn from this figure is that the formaldehyde was far from exhausted at any of the pH levels studied, i.e., 5, 8, and 10. The unused formaldehyde ranged from 50 to 65% of that charged, in contrast to the high proportion fixed in the case of glutaraldehyde. The rate of attainment of maximum T_s was also lower in the case of formaldehyde.

The rate of tanning with glyoxal is shown in Fig. 8. In accordance with Gustavson's conclusion from shrinkage temperature data (14), there was no fixation of glyoxal at a pH of about 5. A gradual fixation of aldehyde and increase in T_s was noted at pH of about 8.

A comparison of these three aldehydes at a pH of about 8 and at a concentration equivalent to 12% glutaraldehyde is shown in the plot of Fig. 9. As judged by the slope of the curves, the rate of tanning increased in the order: glyoxal, formaldehyde, glutaraldehyde. The rate of increase in T_s also followed this same order. Only in the case of glutaraldehyde was exhaustion of aldehyde from the tanning liquor noted.

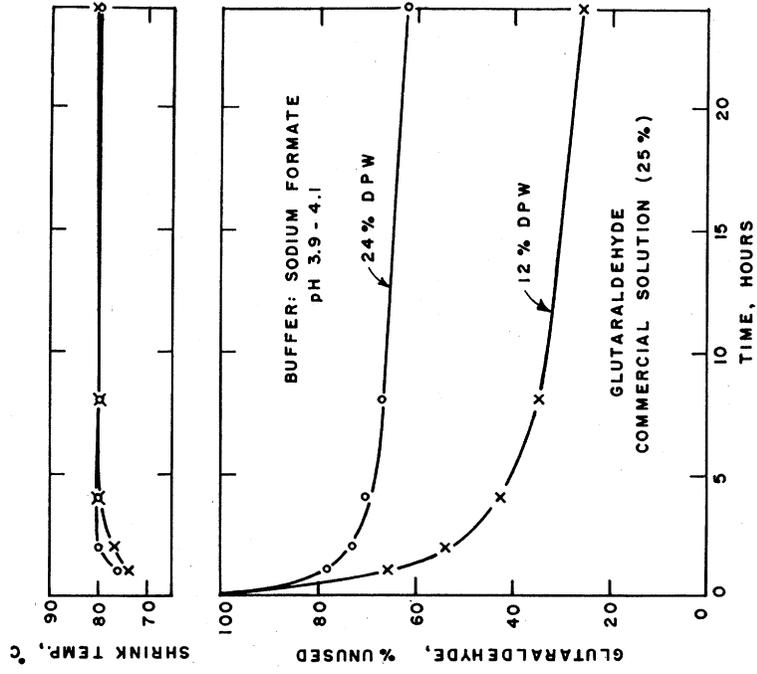


FIGURE 2.—Tanning rate with glutaraldehyde, pH 3.9-4.1

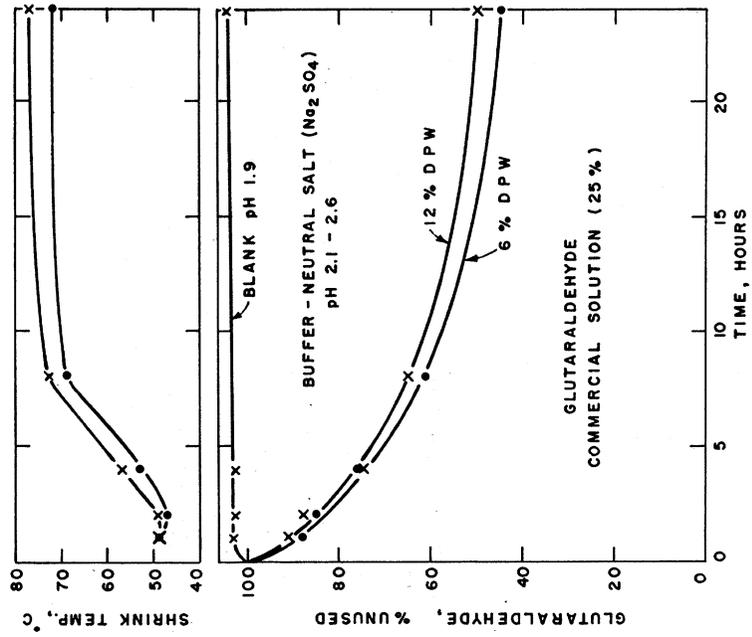


FIGURE 1.—Tanning rate with glutaraldehyde, pH 2.1-2.6

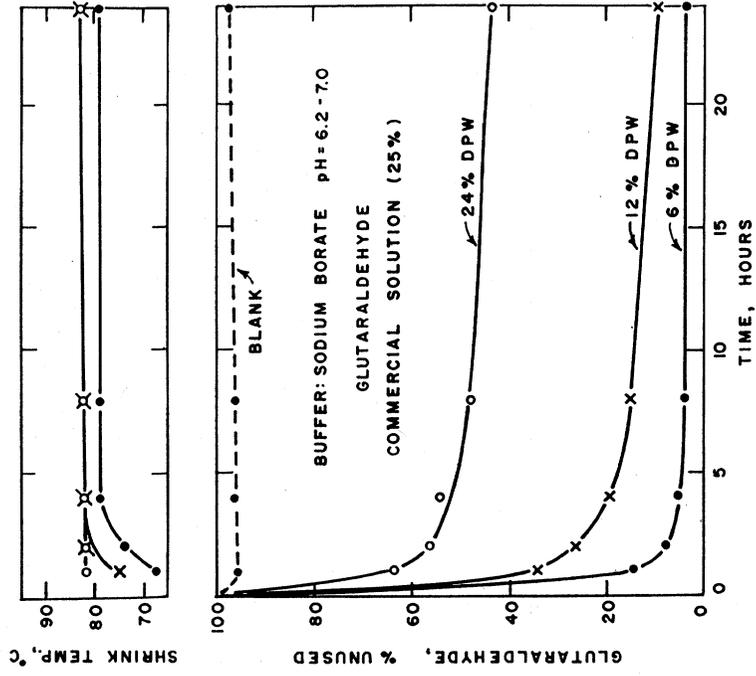


FIGURE 4.—Tanning rate with glutaraldehyde, pH 6.2-7.0

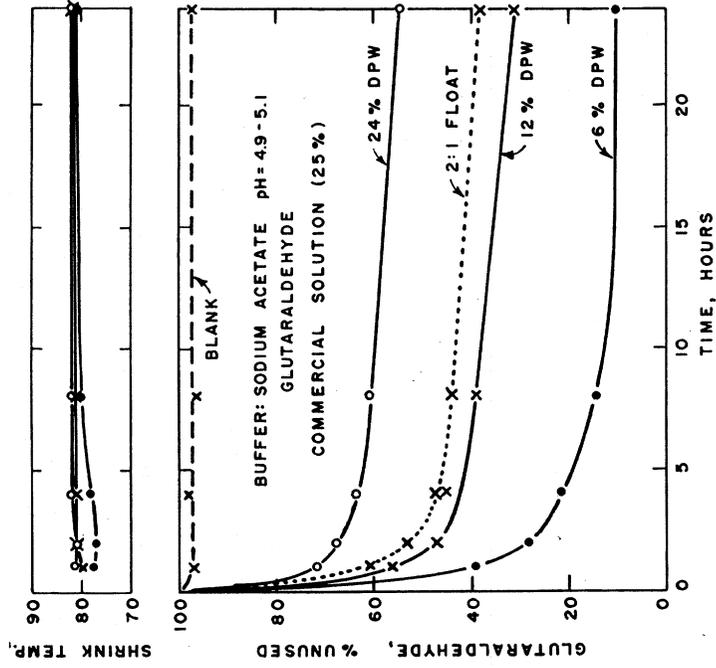


FIGURE 3.—Tanning rate with glutaraldehyde, pH 4.9-5.1

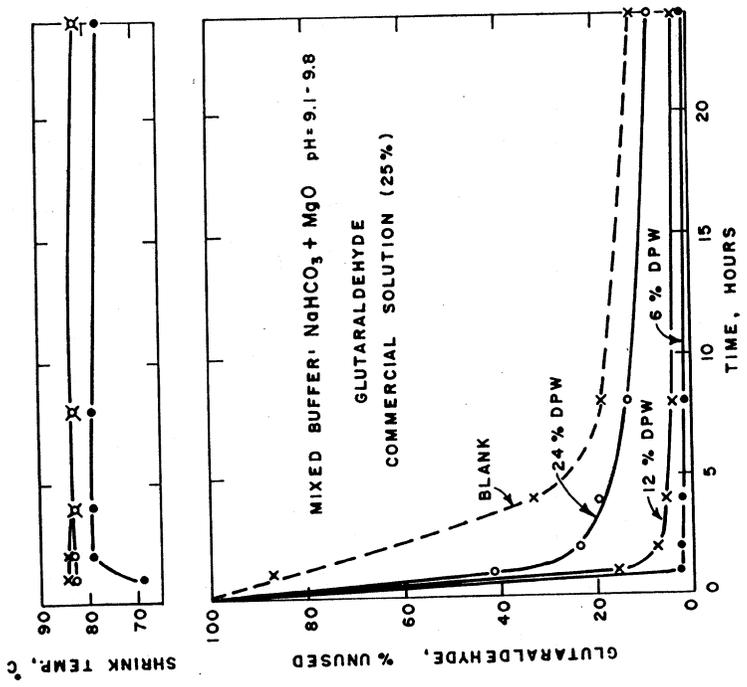


FIGURE 5.—Tanning rate with glutaraldehyde, pH 7.6-8.4

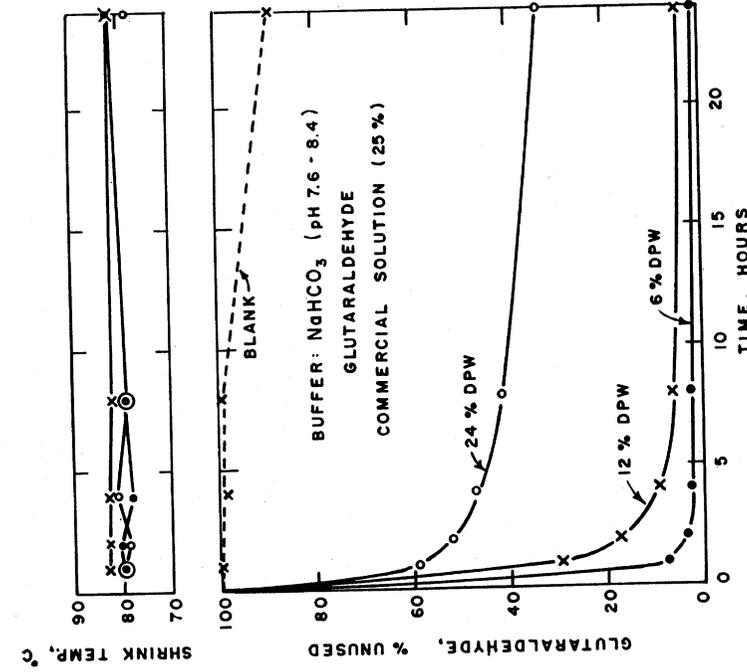


FIGURE 6.—Tanning rate with glutaraldehyde, pH 9.1-9.8

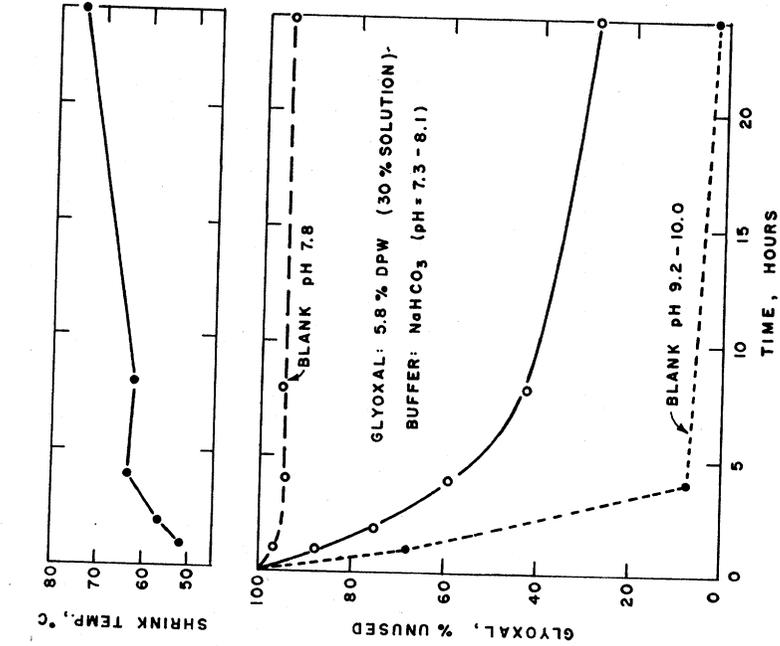


FIGURE 7.—Tanning rate with formaldehyde

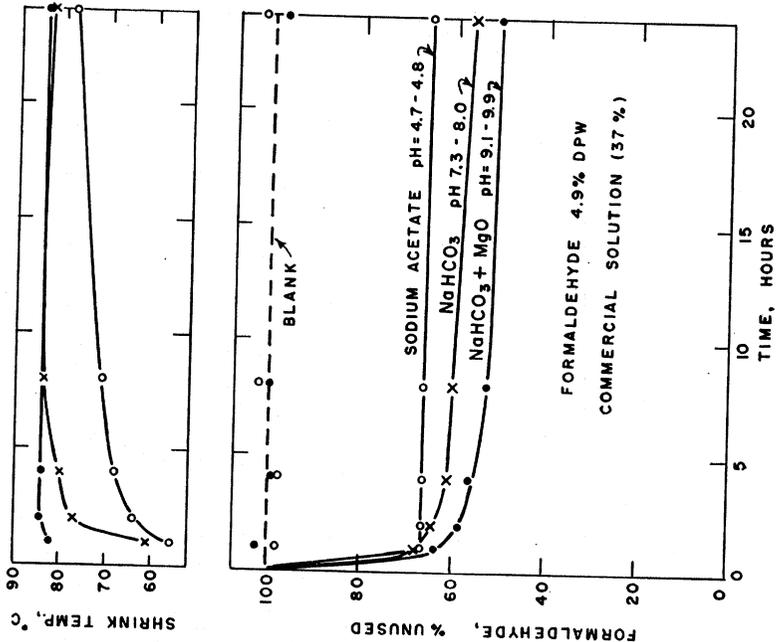


FIGURE 8.—Tanning rate with glyoxal

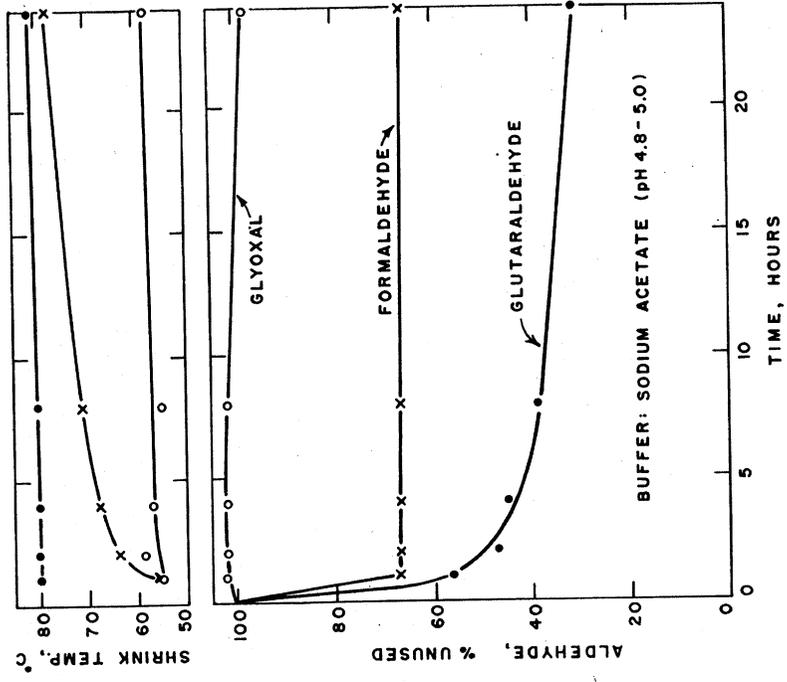


FIGURE 10.—Comparison of rates of tanning at pH 5 (approximately)

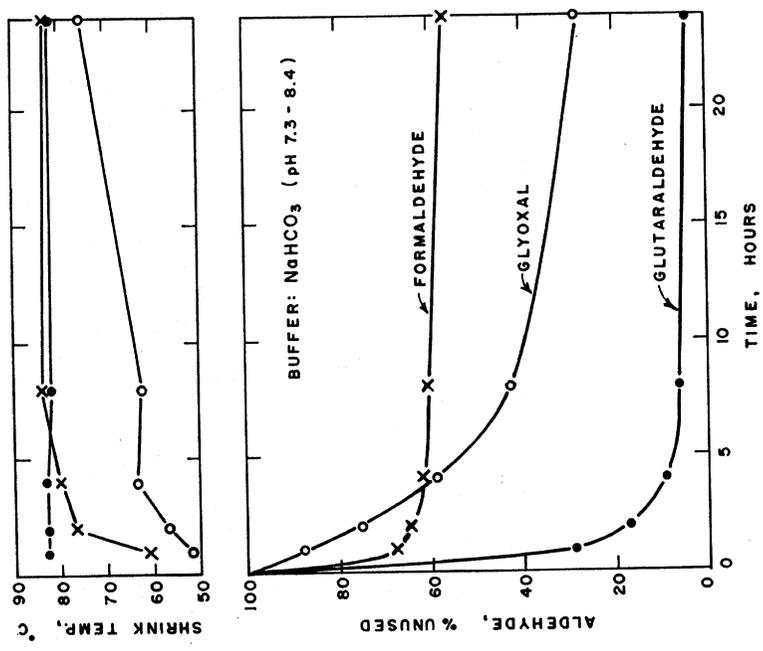


FIGURE 9.—Comparison of rates of tanning at pH 8 (approximately)